

# <sup>13</sup>C NMR spectrum of crystalline [Rh(Acac)(CO)<sub>2</sub>]: a contribution to the discussion on [Rh(Acac)(CO)<sub>2</sub>] structure in the solid state

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## Abstract

<sup>13</sup>C MAS NMR spectrum of polycrystalline [Rh(Acac)(CO)<sub>2</sub>] (**1**) displays separate signals from all 7 carbon atoms: 2 doublets from CO ligand carbons along with 5 singlets from Acac carbons. GIPAW calculation of <sup>13</sup>C shielding tensor values also revealed nonequivalence of all carbon atoms in molecule **1** in the anisotropic medium of the crystal lattice. Apparently, the C<sub>2v</sub> symmetry of molecule **1** is broken owing to the asymmetry of its contacts to the neighboring molecules. For example, the contacts O···H–C of two CO ligands of molecule **1** to the CH group of the closest molecule in the adjacent stack are markedly different: the distances OH are 2.72 and 4.38 Å, OC are 3.65 and 5.00 Å, the angles OHC are 164.9° and 126.4°.

**Keywords:** Rhodium(I) complexes, Carbonyls, Solid-state <sup>13</sup>C NMR, GIPAW calculations, X-ray structure

## **1. Introduction**

Rhodium(I) β-diketonato dicarbonyl complexes, [Rh(Diketo)(CO)<sub>2</sub>], were first prepared in 1964 [1]. These complexes and dozens of their analogs, [Rh(LL)(CO)<sub>2</sub>], containing a variety of bidentate monoanion ligands (LL)<sup>–</sup> with donor atoms {O,O}, {O,N}, {N,N},{O,S}, were synthesized during the following five decades. Acetylacetonate dicarbonyl rhodium(I), [Rh(Acac)(CO)<sub>2</sub>] (**1**), the chronologically and typologically first compound of the group, still continues to attract vivid interest: for applications of **1** in catalysis see monographs [2-6] and

recent research publications [7-13]; for other aspects of its chemistry and physics see [14-36]. X-Ray data on the stacked crystalline structures of **1** and a variety of its analogs were summarized and discussed in [37] with a focus on the metallophilic interactions producing one-dimensional metallic chains. Modern methods of computational chemistry were employed to study the bond situation in complex **1** and examine some of its reactions [38-41].

According to the X-ray diffraction data obtained initially in 1967 [42] and then refined in 1974 [43], the crystal of **1** belongs to the  $P\bar{1}$  space group with two molecules in the triclinic unit cell. Modern study [37] as well as our X-ray data (see Supplementary data) confirmed this attribution. The single crystal IR study reported in 1974 [44] revealed, however, that the number of carbonyl ligand stretching bands in the spectrum of **1** (3 absorption maxima) does not conform to the selection rules for  $P\bar{1}$  symmetry with  $Z = 2$ . To rationalize this finding, authors [44] introduced the concept of “a vibrationally effective cell of orthorhombic symmetry”. Further analysis of IR spectra of polycrystalline **1** at varying degree of  $^{13}\text{C}$  enrichment led us to a conclusion that the unit cell of **1** crystal has no inversion center and thus cannot be assigned to the  $P\bar{1}$  space group. This conclusion has been verified by the observation of the second harmonic generation (SHG) in a polycrystalline sample of **1** [45]. (It should be mentioned that in [14] no SHG from polycrystalline **1** has been observed).

In addition, behavior of  $\nu(\text{CO})$  bands in the spectrum of crystalline **1** upon varying of  $^{13}\text{C}$  enrichment suggested that the carbonyl groups in the molecule **1** are non-equivalent in the solid state [45], and their force constants ( $10^2 \text{ Nm}^{-1}$ ) differ noticeably: 16.88 and 16.58. Here we report on the  $^{13}\text{C}$  MAS NMR spectrum of crystalline **1** and discuss molecular structure of **1** in the solid state using the results of the new X-ray study carried out specifically for this work. The data were initially presented in the form of electronic poster [46].

## 2. Results and discussion

Proton decoupled carbon-13 NMR spectrum of **1** enriched with  $^{13}\text{C}$  (~ 20 %) in carbonyl ligands is presented in the Fig. 1 ( $\text{CDCl}_3$  solution). Numbering of carbon atoms and assignments of their resonances are also depicted therein.  $^{13}\text{CO}$  ligand in the monosubstituted isotopomer,  $[\text{Rh}(\text{Acac})(^{12}\text{CO})(^{13}\text{CO})]$  (predominant one at 20% enrichment), shows one sharp doublet the spectral parameters of which,  $\delta \text{ } ^{13}\text{C}$  183.8 ppm and  $^1\text{J}(\text{CRh})$  73.0 Hz, agree well with the values given for **1** in [47]. The chemical shift values obtained for Acac ligand carbons are also in good

agreement with the data [47]. It should be noted that all three signals from Acac carbons, C<sup>1,3</sup> at 187.4 ppm, C<sup>2</sup> at 101.8 ppm, and C<sup>4,5</sup> at 27.1 ppm, defined in [47] as singlets show not large but distinct doublet splitting in the Fig. 1 spectrum.

<sup>13</sup>C MAS NMR spectra of polycrystalline **1** samples vary in details from one experiment to another, which may be caused by possible irregularities in the crystal lattice and some instrumental artifacts (magnetic field inhomogeneity, sample temperature drift and gradient, imperfect magic angle setting, *etc.*). Despite these variations in the lineshapes and relative intensities of peaks, the overall patterns of the obtained spectra exhibit a recognizable leitmotif which is exemplified below with the spectrum Fig. 2.

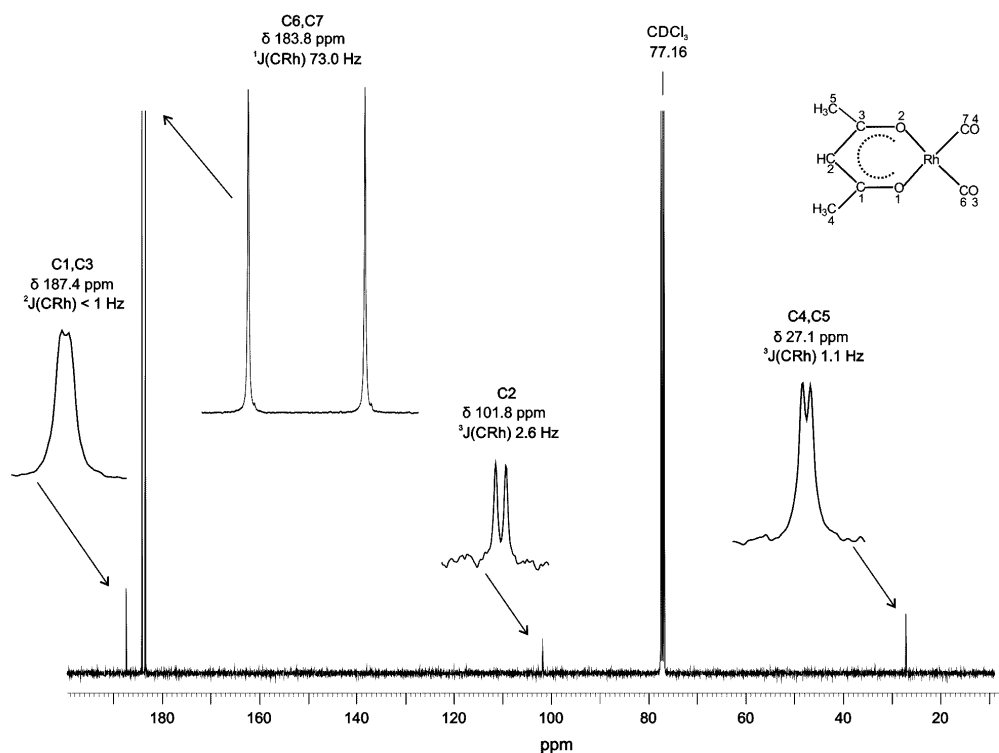


Fig. 1. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of [Rh(Acac)(CO)<sub>2</sub>] (**1**) (<sup>13</sup>CO enrichment ~ 20%) in the CDCl<sub>3</sub> solution.

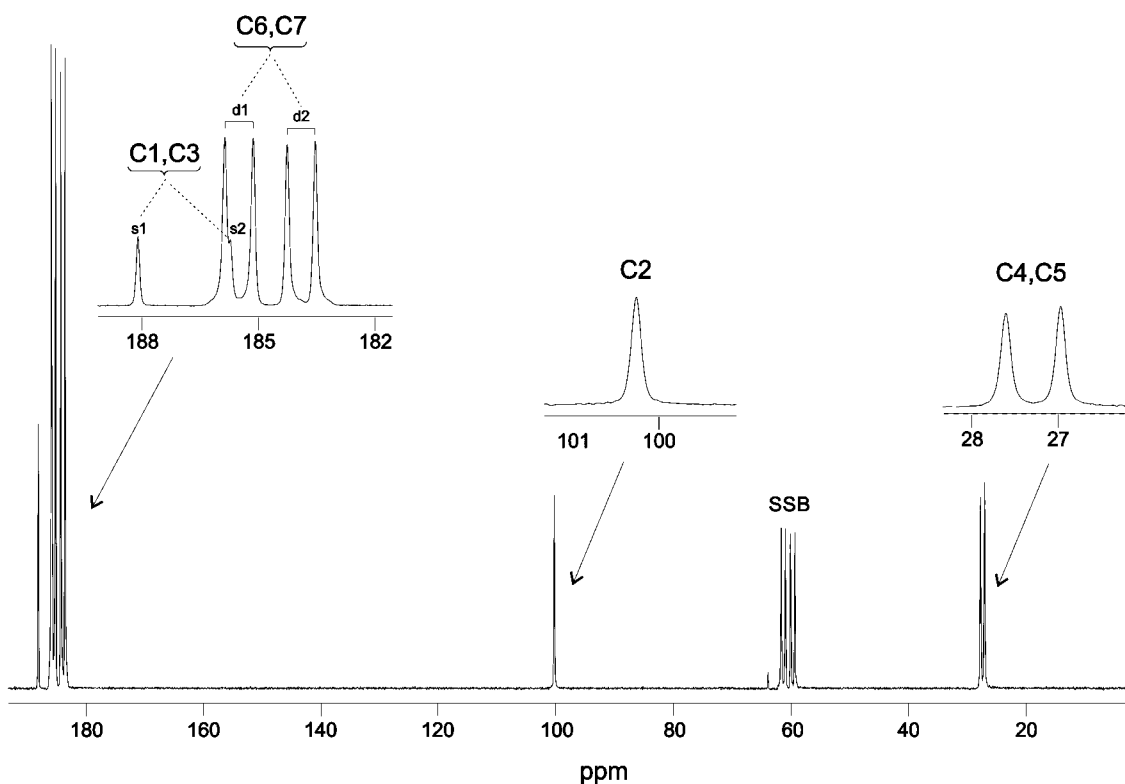


Fig. 2.  $^{13}\text{C}$  MAS NMR spectrum of polycrystalline  $[\text{Rh}(\text{Acac})(\text{CO})_2]$  (**1**) ( $^{13}\text{C}$  enrichment  $\sim 20\%$ ).

Two doublets marked as d1 (185.5 ppm,  $J(\text{CRh}) = 73.3$  Hz) and d2 (183.9 ppm;  $J(\text{CRh}) = 72.8$  Hz) are signals of carbonyl ligand carbons, C6 and C7. Singlets s1 (188.1 ppm) and s2 (185.7 ppm) correspond to carbonyl carbons of Acac ligand, C1 and C3. Acac part of the spectrum, along with the last two signals, contains two singlets from non-equivalent methyl carbons, C4 and C5, (27.7 ppm and 27.0 ppm) and the sole signal (100.3 ppm) from methine carbon, C2 (see Table 1). The assignment of signals inside the pairs of correlative atoms, C1 vs. C3, C4 vs. C5, and C6 vs. C7, remains uncertain. SSB is a spinning side band corresponding to s1, s2, d1 and d2 signals at MAS rotation speed of 12.5 kHz. The weak splittings  $J(\text{CRh}) \sim 1 - 3$  Hz of Acac signals observed in the solution spectrum are not resolved in the spectrum of crystal due to large line widths,  $\sim 10 - 15$  Hz.

Duplication of the  $^{13}\text{C}$  resonances in the solid-state spectrum may be caused by irregularities in the crystal structure of **1**. In this regard, it is appropriate to recall the remark of

the authors [43] in their overall description of the polycrystalline mass of **1**: “A peculiar feature was the frequency with which curved crystals were found, some even being s-shaped.” These abnormalities in the habitus of crystals should be related to certain distortions in their internal structure, for instance to the formation of twinned crystals. In this case, the correlative carbons of Acac ligand, ( $C^1$  and  $C^3$ ), ( $C^4$  and  $C^5$ ), as well as carbons ( $C^6$  and  $C^7$ ) of carbonyl ligands within the same molecule **1** remain equivalent but each component of a twinned crystal produces its own set of  $^{13}\text{C}$  resonances. Alternative (and perhaps more plausible) cause for the duplication of the  $^{13}\text{C}$  resonances may be breaking of the  $C_{2v}$  molecular symmetry when molecule **1** passes from the solution into the crystal. In this case, every molecule of **1** in the crystalline state contains two non-equivalent carbonyl ligands and two unequal parts of Acac ligand. This last understanding is appropriate both for the perfect crystalline structures and for distorted ones. Non-equivalence of carbonyl ligands in molecule **1** may result from difference in their close surroundings in the crystal lattice. In particular, X-ray data show that the contacts  $\text{O}\cdots\text{H}-\text{C}$  of two carbonyl oxygens,  $\text{O}^3$  and  $\text{O}^4$ , to methyl and methine protons of the neighboring molecules are markedly different (see Supplementary data, Table 6S). This may be illustrated by a comparison of the  $\text{O}^3$  and  $\text{O}^4$  contacts to the same partner, methine group  $\text{C}^{2a}\text{H}^{2a}$ , of the closest neighboring molecule (marked with an “a”) belonging to the adjacent stack:

distance  $\text{O}^3\cdots\text{H}^{2a}$  2.72 Å; distance  $\text{O}^3\cdots\text{C}^{2a}$  3.65 Å; angle  $\text{O}^3\text{H}^{2a}\text{C}^{2a}$  164.9°  
distance  $\text{O}^4\cdots\text{H}^{2a}$  4.38 Å; distance  $\text{O}^4\cdots\text{C}^{2a}$  5.00 Å; angle  $\text{O}^4\text{H}^{2a}\text{C}^{2a}$  126.4°

Noteworthy is that the values of contact parameters for  $\text{O}^3$  meet the IUCr criteria for a weak hydrogen bond: “A longer  $\text{C}-\text{H}\cdots\text{O}$  contact ( $D > 3.6$  Å) may be acceptable as a hydrogen bond if the angle tends towards linearity ( $\theta > 150^\circ$ )” [48]. Further, due to the transmission of carbonyl ligand electronic effects through the central atom, the pairwise correlative carbons of Acac ligand, ( $C^1$  and  $C^3$ ), ( $C^4$  and  $C^5$ ), also become non-equivalent. Under this assumption, we can say that molecule **1**, on passing into the crystal, retains the  $C_{2v}$  symmetry with regard to its geometry, but loses that symmetry with regard to subtle characteristics of atoms and bonds. Some features of the  $^{13}\text{C}$  NMR spectrum presented in Fig. 2 support this understanding: 1) the peak corresponding to the only unpaired carbon atom,  $C^2$ , is not duplicated; 2) the peaks from the pairwise correlative carbons of Acac ligand (for instance,  $C^4$  and  $C^5$ ) are of equal intensity.

Inspection of CIF file for previously published structure of **1** ([43], CSD refcode ACABRH02) showed the same difference between O<sup>3</sup> and O<sup>4</sup> contacts. Parallel results were obtained also for iridium analog of **1**, [IrAcac(CO)<sub>2</sub>] ([49], CSD refcode ACRHCO02).

Furthermore, we calculated shielding tensor values in the solid-state <sup>13</sup>C NMR spectrum of **1** by means of GIPAW method. Two models were constructed for these calculations. The first one, GIPAW(X-ray), corresponded to the experimental crystal structure with C-H distances normalized according to the neutron diffraction value (1.083 Å). In the second model, GIPAW(OptGeom), the structure with optimized coordinates of all atoms was used (the cell parameters were fixed to the experimental values). The two models gave very similar results, both with markedly overestimated values of <sup>13</sup>C chemical shift for carbonyl ligand carbons, C<sup>6</sup> and C<sup>7</sup> (Table 1).

Table 1. Experimental and calculated <sup>13</sup>C chemical shifts in **1**.

Atom label	$\delta^{13}\text{C}$ , ppm		
	Calculated		Experimental
	GIPAW(X-ray)	GIPAW(OptGeom)	
C1	189.7	191.0	188.1 and 185.7
C3	187.4	188.8	
C2	106.1	107.8	100.3
C4	29.0	30.7	27.7 and 27.0
C5	27.9	29.6	
C6	203.2	208.8	185.5 and 183.9
C7	204.0	207.3	

It can be seen that the GIPAW(OptGeom) procedure led to larger <sup>13</sup>C values as compared to the GIPAW(X-ray) procedure. This situation is common for DFT calculations of solid-state NMR spectra of organic and organometallic compounds by GIPAW method [50].

In the context of this paper, it is essential that, according to the computation results, the pairwise correlative carbon atoms (C<sup>1</sup> and C<sup>3</sup>; C<sup>4</sup> and C<sup>5</sup>; C<sup>6</sup> and C<sup>7</sup>) are nonequivalent, which supports our assumption that duplication of <sup>13</sup>C resonances in the solid-state spectrum is caused by the breaking of the C<sub>2v</sub> symmetry of the molecule **1** on passing from the solution to the crystal. It can be also noticed that the differences between calculated  $\delta^{13}\text{C}$  values within these pairs (which may be considered as a measure of the carbon atoms non-equivalence) are close to the respective differences between experimental values.

### 3. Conclusion

$^{13}\text{C}$  NMR study of crystalline  $[\text{RhAcac}(\text{CO})_2]$  (**1**) suggests non-equivalence of the pairwise correlative carbon atoms in molecule **1** ( $\text{C}^1$  vs.  $\text{C}^3$ ;  $\text{C}^4$  vs.  $\text{C}^5$ ;  $\text{C}^6$  vs.  $\text{C}^7$ ). DFT calculation of solid-state NMR spectra supports this understanding. Apparently, the  $\text{C}_{2v}$  symmetry of the electron density distribution in molecule **1** is broken in the crystalline state owing to the difference in the closest surroundings of carbonyl ligands.

### 4. Material and methods

$[\text{RhAcac}(\text{CO})_2]$  (**1**) was prepared by published procedure [51]. The  $^{13}\text{C}$  enriched **1** was prepared by action of 50% enriched  $^{13}\text{CO}$  gas on a solution of  $[\text{Rh}(\text{Acac})(\text{CO})_2]$  in benzene.

100 MHz carbon-13 NMR spectra were measured at room temperature on spectrometers Bruker Avance III 400 ( $^{13}\text{C}\{^1\text{H}\}$ , solution in  $\text{CDCl}_3$ ) and Avance III 400WB ( $^{13}\text{C}$  MAS, polycrystalline sample). Typical conditions for solid-state NMR were as follows: 4 mm rotor, standard Bruker *cp* pulse program, spinning rate 12.5 kHz,  $^1\text{H}$   $90^\circ$  pulse 2.5  $\mu\text{s}$ , contact time 8 ms, recycle delay 60 s, number of acquisitions 512. Chemical shifts are referenced to tetramethylsilane. NMR studies were performed at the Centre for Magnetic Resonance, St. Petersburg State University.

DFT calculations of solid-state NMR spectra were performed within the PBE exchange-correlation functional using VASP 5.4.1 program [52-55]. Atomic cores were described using PAW potentials, while valence electrons were described by plane wave basis set, kinetic energy cutoff being equal to 800e. To solve Kohn-Sham equations,  $4\times 4\times 4$  Monkhorst-Pack k-point grid [56] was used. Computation of  $^{13}\text{C}$  shielding tensors in the crystalline **1** was carried out using GIPAW method [57].

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